

# SCIENCE FOR GLASS PRODUCTION

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## MECHANICAL ACTIVATION OF BATCH AS A METHOD OF INCREASING GLASS STRENGTH

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The effect of mechanical activation of glass batch on the glassmaking process and on the mechanical strength of glass is studied. It is shown that dry-grinding of the batch to specific surface area  $1.1 \text{ m}^2/\text{g}$  decreases the silicate and glass formation temperatures by  $100 - 150^\circ\text{C}$ . Mechanical activation of glass batch more than doubles the strength of glass.

**Key words:** mechanical activation, glass batch, glassmaking, strength.

Low operational strength is one of the central problems in using glass as a construction material. The strength of glass can be increased by tempering, ion exchange and etching. These methods are based on compensation of the surface defects, i.e., only one reason for the loss of strength is eliminated. For this reason even when used in combination these methods increase the strength of glass only up to a definite limit ( $1500 - 2000 \text{ MPa}$ ) [1].

Another factor resulting in the loss of strength is the presence of stress concentrators in the interior of the glass. Therefore, another resource for increasing strength should be sought in obtaining molten glass of the highest possible homogeneity and preserving the uniformity during all technological process stages. Aside from optimizing the temperature-time parameters of melting and producing glass this problem can be solved by increasing the homogeneity and glassmaking capacity of the glass batch. This can be accomplished by combined fine milling of the raw materials [2].

The modern milling apparatus used in related industries make it possible to obtain particles with diameters of several microns [3, 4]. As a result of combined fine milling of the components a significant part of the homogenization process should be carried over from the furnace to the batch preparation stage. On the other hand fine milling is associated with an intense mechanical effect on the material, which becomes chemically more active [5, 6]. This phenomenon is well known in chemical technology as ‘mechanical activation’. In application to glassmaking technology an increase in the ac-

tivity of the initial material should accelerate the glassmaking process and lower the formation temperature of the glass melt.

Our objective in the present work was to study the particulars of the physical-chemical processes occurring during melting of mechanically activated glass batch and to evaluate the effect of the mechanical activation on the strength of the glass obtained.

The effect of mechanical activation of batch on the temperature ranges of the glassmaking and melting stages as a whole was studied for glass batch with composition close to sheet glass. The raw materials were quartz sand (VS-050-1), sodium nitrate (granulated, chemical grade) and calcium carbonate (powder, chemical grade). The initial material was passed through a No. 08 sieve. An MP/4×0.5 planetary mill was for mechanical activation of the glass batch. The milling was performed by the dry method. The milling time was 60 min, since subsequent comminution resulted in complete aggregation of the batch. The specific surface area of the powder obtained was determined by the air-permeability method (PSKh-11(SP)) and was equal to  $1.1 \text{ m}^2/\text{g}$ . Microscopic study of the obtained batch showed that the grain size of the raw components does not exceed  $10 \mu\text{m}$  with the main fraction about  $2 \mu\text{m}$ .

The sequence of phase transformations in the initial and activated batch was studied by differential scanning calorimetry (Netzsch STA 449c). For an exhaustive interpretation of the processes occurring during melting of the experimental batches, these batches were heat-treated at the tempera-

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**TABLE 1.** Physical-Chemical Processes Occurring in Heated Unactivated Batch

Heat effect	Temperature, °C	Process
Endo	To 200	Removal of physically and chemically bound water
Endo-min	571	Polymorphic transformation $\alpha$ -quartz $\rightarrow$ $\beta$ -quartz
Endo	760 – 830 $t_{\min} = 810$	Chemical interaction at grain contact sites with formation of $\text{Ca}_2\text{SiO}_4$ and $\text{Na}_2\text{Si}_2\text{O}_5$
Endo	840 – 920 $t_{\min} = 890$	Intense chemical interaction with formation of $\text{Na}_2\text{CaSi}_3\text{O}_8 + \text{Na}_2\text{CaSiO}_4$
Endo	> 1000	Melting of eutectic, partial cristobalitization of quartz, dissolution of unreacted components
Absent	> 1300	X-ray amorphous melt

tures 675, 725, 800, 900, 950, 1000, 1100, 1200, 1300, 1400 and 1500°C. The samples obtained were studied visually and by x-ray phase analysis (DRON-3M with copper anode). The results are colligated in Tables 1 and 2.

The differences in the behavior of comminuted and non-comminuted batches start to manifest at temperatures > 300°C. The formation of double carbonates is observed in activated but not unactivated batch. This can be explained by a scale factor – the presence of a developed surface of contact between phases in the fine-milled batch makes it possible for the corresponding reactions to go to completion. In conventional granulometry this interaction is possible only on a very limited contact area of quite large particles, which does not allow any significant yield of reaction products. For the same reasons separate formation of  $\text{Ca}_2\text{SiO}_4$  and  $\text{Na}_2\text{Si}_2\text{O}_5$  on the interphase boundaries  $\text{Na}_2\text{CO}_3$ – $\text{SiO}_2$  and  $\text{CaCO}_3$ – $\text{SiO}_2$ , respectively, is observed in unactivated batch, while in activated batch double carbonates at temperatures more than 150°C lower than in unactivated batch immediately form double silicates on reacting with  $\text{SiO}_2$ . This temperature shift could be associated in part with the lower temperatures of interaction of double carbonates with  $\text{SiO}_2$  as compared with  $\text{Na}_2\text{CO}_3$  and  $\text{Ca}_2\text{CO}_3$  [7, 8]. Differential scanning calorimetry revealed that for activated batch the area of the endo effect of the transition  $\alpha$ -quartz  $\rightarrow$   $\beta$ -quartz is smaller compared with unactivated batch.

At 840 – 920°C double silicates form directly from the remaining unreacted carbonates,  $\text{SiO}_2$  and sodium and calcium silicates in the uncomminuted batch. The same process occurs in the comminuted batch at 700 – 830°C. At temperatures near 800°C the decomposition of carbonates in the activated batch is completed and the lowest-melting eutectics melt [9, 10]. An exo effect is recorded on the DSC curve for the comminuted batch in the temperature interval 850 – 960°C, and x-ray diffraction analysis reveals the presence of a wollastonite phase, which, in all probability, indicates that

**TABLE 2.** Physical-Chemical Processes Occurring in Heated Batch Activated by Dry Milling

Heat effect	Temperature, °C	Process
Endo	To 200	Removal of physically and chemically bound water
Endo-min	378	Formation of $\text{Na}_2\text{Ca}_2(\text{CO}_3)_3$
Endo-min	435	Formation of $\text{Na}_2\text{Ca}(\text{CO}_3)_2$
Endo-min	571	Polymorphic transformation $\alpha$ -quartz $\rightarrow$ $\beta$ -quartz
Endo	520 – 690 $t_{\min} = 620$	Chemical interaction of double carbonates with $\text{SiO}_2$ with formation of $\text{Na}_2\text{CaSi}_3\text{O}_8 + \text{Na}_2\text{CaSiO}_4$
Endo	710 – 780 $t_{\min} = 760$	Chemical interaction with formation of $\text{Na}_2\text{CaSi}_3\text{O}_8 + \text{Na}_2\text{CaSiO}_4$
Endo	780 – 830 $t_{\min} = 810$	Final decomposition of the remaining carbonates, melting of eutectic
Exo	850 – 960 $t_{\max} = 900$	Formation of wollastonite-like phase
Endo	1000 – 1100	Dissolution of quartz and wollastonite-like phase
Absent	1100	X-ray amorphous melt

this phase crystallizes from the melt. Indeed, the large quantity of undissolved crystalline inclusions and a possible strong calcium supersaturation of the melt create favorable thermodynamic conditions for the phenomenon under study.

At 1100°C the dry-milled batch forms a completely x-ray amorphous melt but with a large number of gas bubbles. The uncomminuted batch at 1100°C remains opaque, and numerous crystalline inclusions, which completely dissolve at temperatures  $\geq 1300^\circ\text{C}$ , are observed in it. A high-quality fined melt was obtained only for activated batch at 1500°C.

There are a number of reasons why in terms of the temperature intervals of silicate and glass formation the activated batch significantly leads the unactivated batch. In the first place, there is the effect of the scale factor in the heterogeneous interaction. Grain-size reduction in the batch gives the following: a large contact area of the interacting substances, large initial homogenization of the mixture, smaller thickness of the layer of reaction products (which partially levels the effect of low diffusion rates). This increases the yield of reaction products and the fraction of components combining in eutectic proportion. In the second place, it is a result of mechanical activation. It is known that the low chemical activity of quartz sand is a limiting factor, determining the rate of silicate and glass formation [7]. During milling in a planetary mill the sand grains undergo repeated impacts. Initially, the energy of the collisions is mostly expended on the destruction of the particles, which increases the relative fraction of uncompensated surface bonds possessing elevated chemical activity. As the particle size de-

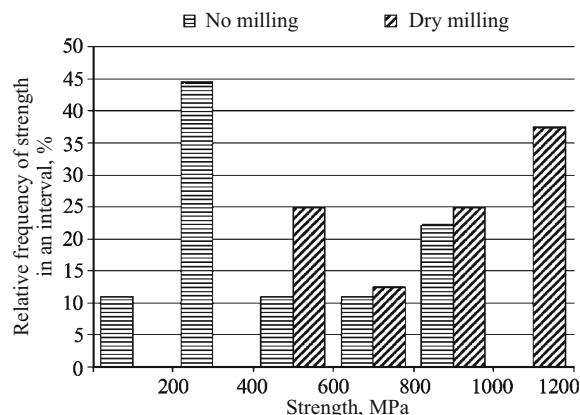


Fig. 1. Differential strength distribution functions for glass made from activated and unactivated batch.

creases, the impact energies become too low for a new surface to form, and part of this energy is stored in the material in the form of defects in the crystal lattice and part is dissipated [5, 6]. The accumulation of structural defects results in a significant increase of the internal energy of material and manifests in a reduction of the energy expenditure on phase transitions, dissolution and chemical reactions.

In summary, the intensifying effect of drying milling of the batch on the physical-chemical processes occurring during glassmaking was confirmed at the first stage of the present investigation. The activating effect of fine milling is manifested in a significant shift by 100 – 150°C of the silicate and glass formation processes into the low-temperature region as compared with the uncomminuted batch as well as in some change in the interaction of the components on heating.

To determine the effect of the activation of the batch on the strength of the glass a large amount of molten glass (10 kg of glass) was made from the dry-activated and inactivated batches. To eliminate incomplete fining in a large volume melt the glass was melted in an induction furnace placed in a vacuum chamber. The melting was conducted at 1500°C and normal pressure while the fining was conducted in a vacuum of 1 atm. The ready fined glass was formed by casting and annealed in a muffle furnace at 600°C. Next, the blanks obtained were positioned, spaced, ground and polished to dimensions 60 × 60 × 3.5 mm.

To prevent surface defects from affecting the strength of the glass the samples were etched in a mixture of sulfuric and hydrofluoric acids to depth 250 μm. To prevent the reappearance of surface microdefects a polymer coating was deposited on the etched surface. The glass was tested for strength by means of centro-symmetric bending. The results of these tests are presented in Fig. 1.

Statistical analysis of the data obtained showed a significant increase in strength for glass made from dry-milled batch. The average strength is  $320 \pm 160$  MPa for unactivated batch and  $820 \pm 225$  MPa for activated batch. In addition, there are serious differences in the strength limits: min 145, max 920 and min 450, max 1120 MPa for unactivated and activated batch, respectively.

Conventional granulometry of the batch presupposes grain composition in the range 0.3 – 1.5 mm for the main forms of raw material. This sets the scale of the initial nonuniformities of the melt at 100 microns. At the same time the viscosity of the melt  $10 - 10^2$  Pa · sec impedes the formation of turbulence during the motion of the molten glass and limits the homogenization range on the diffusion intensity side.

The combined fine milling of the raw materials secures the primary homogenization of the batch at the microlevel and significantly intensifies the entire glassmaking process. Thus, favorable conditions are created for more complete homogenization of the melt than in the case of batch with conventional granulometry. Therefore, such large differences in glass strength are determined solely by the influence of the activation process on the interior defects in the glass.

In practice, mechanical activation of batch will make it possible to at least double the minimum strength of glass.

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